

PATENT SPECIFICATION

NO DRAWINGS

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1,183,854

1,183,854



Date of Application and filing Complete Specification: 14 July, 1967.

No. 32591/67.

Complete Specification Published: 11 March, 1970.

Index at acceptance: —C2 C(1G5B, 1G6B3, 1H1A1, 1H1C3, 1J2A2, 1J2C3, 1J2E, 2D11, 215, 247, 25Y, 250, 252, 31Y, 313, 32Y, 323, 337, 36Y, 360, 361, 45Y, 456, 652, 670, 794, 173-199-272, LE)

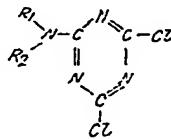
International Classification: —C 07 d 55/46

COMPLETE SPECIFICATION

Brightening Agents of the Bistriazinylaminostilbene Series

We, FARBNENFABRIKEN BAYER AKTIEN-
GESELLSCHAFT, a body corporate organised
under the laws of Germany, of Leverkusen,
Germany, do hereby declare the invention,
5 for which we pray that a patent may be
granted to us, and the method by which it
is to be performed, to be particularly de-
scribed in and by the following statement:—

The present invention relates to an im-
10 provement in the process for the production
of brightening agents of the bis - triazinyl -
aminostilbene series by condensation of 4,4'-
diamino - stilbene - 2,2' - disulphonic acid
15 or salts thereof with amino - dichlorotri -
azine compounds of the general formula



wherein R_1 and R_2 , independently of each
other, stand for a hydrogen atom, or for an
alkyl or hydroxyalkyl group containing 1 to
20 5 carbon atoms or for a carboxyalkyl or alkoxy-
carbonylalkyl group containing 1 to 5 carbon
atoms in the alkyl moiety, or jointly with the
nitrogen, atom, form the morpholine, piperi-
dine or pyrrolidine ring system, in a mole-
25 cular ratio of 1:2, and optionally subsequently
reacting the resulting condensation products
with ammonia or amines; the improvement
consisting in carrying out the condensation
30 of 4,4' - diaminostilbene - 2,2' - disulphonic
acid or salts thereof with the aminodichlorotri-
azine compounds in an aqueous medium
which is free of organic solvents.

Aminodichlorotriazine compounds of the

above formula which are suitable for the
herein described process include the com-
pounds which are obtainable by reacting
cyanuric chloride with ammonia, methyl-,
ethyl- or butylamine, dimethyl-, diethyl- or
dipropylamine, mono- or diethanolamine, N-
methylmethanolamine, aminoacetic acid, amino-
butyric acid or amino caproic acid, amino-
acetic acid ethyl ester or β - aminopropionic
acid ethyl ester or pyrrolidine, piperidine or
morpholine at a molecular ratio of 1:1 in
known manner in an aqueous medium in the
presence or in the absence of organic solvents
for cyanuric chloride and recovering the reac-
tion product from the suspension.

The alkali metal salts are especially suitable
salts of 4,4' - diaminostilbene - 2,2' - di -
sulfonic acid.

The herein described condensation of 4,4'-
diaminostilbene - 2,2' - disulfonic acid or
salts thereof with aminodichlorotriazine com-
pounds in an aqueous medium which is free
of organic solvents is preferably performed
in the presence of acid-binding agents such
as sodium carbonate or sodium bicarbonate
at temperatures between 70—80°C. When
aminodichlorotriazine compounds are applied
which have been prepared by reacting cyanuric
chloride with ammonia or the
amines in an aqueous medium in the absence
of organic solvents for cyanuric chloride, the
suspension obtained can be used for the con-
densation directly.

In many cases it has proved advantageous
to perform the condensation according to the
invention in the presence of a wetting agent.
Suitable wetting agents are for example the
reaction products of 1 mol of fatty alcohol
with 5—8 mols of ethylene oxide as well
as the alkali metal or ammonium salts of

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the acidic sulfuric acid esters of such reaction products.

Suitable amines which may be used in the optionally performed subsequent reaction of the condensation products obtained according to the invention are e.g. methylamine, di-methylamine, ethylamine, diethylamine, mono-ethanolamine, diethanolamine, N - methyl - ethanolamine, morpholine, piperidine, pyrrolidine, aniline, chloroaniline, toluidine, sulfanilic acid, metanilic acid, aminobenzoic acids, taurine and N - methyl - taurine.

The brightening agents of the bistriazinylaminostilbene series which are obtained according to the invention are more effective than the brightening agents of the bistriazinylaminostilbene series which are prepared by condensation of 4,4' - diamino - stilbene - 2,2' - disulfonic acid or salts thereof with the corresponding aminodichlorotriazine compounds of the above formula in conventional manner in an aqueous medium containing organic solvents. This is in particular true if the aminodichlorotriazine compounds are used in the condensation according to the invention after purification for example by washing or recrystallizing.

The invention is further illustrated by the following Examples without being restricted thereto, the parts given being parts by weight if not otherwise stated.

EXAMPLE 2

18.6 parts of the disodium salt of 4,4' - diaminostilbene - 2,2' - disulfonic acid, 25.3 parts of 2 - diethanolamino - 4,6 - di-chloro - 1,3,5 - triazine and 7.6 parts of sodium bicarbonate are introduced, while stirring, into 150 parts of water containing 0.5 part of a wetting agent prepared by reacting 5 mols of ethylene oxide and 1 mol of dodecyl alcohol. The mixture is stirred at 75°C for 90 minutes; the resulting solution is then filtered while hot. Upon cooling the disodium salt of the 4,4' - bis - [2 - diethanol - amino - 4 - chloro - 1,3,5 - triazinyl - (6) - amino] - stilbene - 2,2' - disulfonic acid crystallizes; yield: 36.5 parts, i.e. 96% of the theoretical calculated on the disodium salt of the 4,4' - diamino - stilbene - 2,2' - disulfonic acid used.

The 2 - diethanolamino - 4,6 - dichloro - 1,3,5 - triazine used in the above described Example is prepared as follows:

37 parts of cyanuric chloride are introduced at room temperature into 200 parts of water to which 1 part of the reaction product of 5 mols of ethylene oxide and 1 mol of dodecylalcohol has been added as wetting agent. A solution of 45 parts of diethanol - amine in 155 parts of water are added to the suspension, while stirring, within 30 minutes. The temperature rises to 35°C. The reaction mixture is then heated to 40°C for 30 minutes whereupon the pH value drops to 7. The

resulting 2 - diethanolamine - 4,6 - di - chloro - 1,3,5 - triazine is filtered off, washed with methylethylketone and recrystallized from methylethylketone; 45 parts are obtained; melting point 139°C.

EXAMPLE 2

18.6 parts of the disodium salt of the 4,4' - diaminostilbene - 2,2' - disulfonic acid, 22.3 parts of 2 - [N - methylethanolamino] - 4,6 - dichloro - 1,3,5 - triazine and 7.6 parts of sodium bicarbonate are stirred at 80°C in 200 parts of water containing 0.5 part of the wetting agent indicated in Example 1 until the reaction is negative on diazotizable amine. The solution which is now clear is cooled. The disodium salt of the 4,4' - bis - [2 - N - methylethanolamino - 4 - chloro - 1,3,5 - triazinyl - (6) - amino] - stilbene - 2,2' - disulfonic acid crystallizes. Yield: 33.6 parts, i.e. 95% of the theoretical calculated on the disodium salt of the 4,4' - diamino - stilbene - 2,2' - disulfonic acid used.

The 2 - [N - methylethanolamino] - 4,6 - dichloro - 1,3,5 - triazine used in the above Example is prepared as follows:

37 parts of cyanuric chloride are stirred at 15°C in 200 parts of water to which 1 part of the reaction product of 5 mols of ethylene oxide and 1 mol of dodecyl alcohol has been added as wetting agent. A solution of 40.6 parts of N - methylethanolamine in 180 parts of water is added, while stirring, to this suspension within 40 minutes, the mixture is then stirred at 15°C for 35 minutes, heated to 60°C and stirred at this temperature for another 35 minutes. The resulting 2 - [N - methylethanolamino] - 4,6 - dichloro - 1,3,5 - triazine is filtered off with suction and washed with water. 42.4 parts are obtained; melting point 88°C.

EXAMPLE 3

18.6 parts of the disodium salt of the 4,4' - diaminostilbene - 2,2' disulfonic acid, 21.9 parts of 2 - pyrrolidino - 4,6 - di - chloro - 1,3,5 - triazine and 7.6 parts of sodium bicarbonate are stirred at 80°C in 200 parts of water containing 0.5 part of the wetting agent indicated in Example 1 until the reaction is negative on diazotizable amine. The reaction mixture is then cooled down and the precipitated disodium salt of 4,4' - bis - [2 - pyrrolidino - 4 - chloro - 1,3,5 - triazinyl - (6) - amino] - stilbene - 2,2' - disulfonic acid is filtered off. Yield: 35 parts, i.e. 99% of the theoretical calculated on the disodium salt of the 4,4' - diaminostilbene - 2,2' - disulfonic acid.

The 2 - pyrrolidino - 4,6 - dichloro - 1,3,5 - triazine used in the above Example is prepared as follows:

37 parts of cyanuric chloride are introduced at room temperature into 150 parts of water to which 1 part of the reaction pro-

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- duct of 5 mols of ethylene oxide and 1 mol of dodecylalcohol have been added as wetting agent. A solution of 14.2 parts of pyrrolidine and 100 parts of water is added to this suspension and the reaction mixture is treated in small portions with 11 parts of sodium carbonate in the course of 1 hour. The reaction product is filtered off with suction, dried in the air and recrystallized from petroleum ether. 38 Parts of 2 - pyrrolidino - 4,6 - dichloro - 1,3,5 - triazine are obtained. Melting point 111—112°C.

EXAMPLE 4

- 18.5 Parts of cyanuric chloride are introduced at room temperature into 100 parts of water containing 0.5 part of the wetting agent indicated in Example 1. The suspension is cooled to 10°C, then mixed, while stirring, at this temperature with a solution of 11 parts of diethanolamine in 40 parts of water in the course of 25 minutes. 10.6 Parts of sodium carbonate are then added in small portions within 10 minutes. The reaction mixture is stirred at 15°C for another 35 minutes and then heated to 60°C for 35 minutes. The aqueous suspension of 2 - diethanolamino - 4,6 - dichloro - 1,3,5 - triazine thus obtained is subsequently treated with a solution of 18.6 parts of the disodium salt of the 4,4' - diaminostilbene - 2,2' - disulfonic acid in 150 parts of water and kept at 75°C for about 60 minutes. The resulting solution is filtered off and cooled. The disodium salt of the 4,4' - bis - [2 - diethanolamino - 4 - chloro - 1,3,5 - triazinyl - (6) - amino] - stilbene - 2,2' - disulfonic acid crystallizes. Yield 36.5 parts.

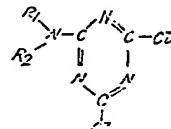
EXAMPLE 5

- 18.5 parts of cyanuric chloride are introduced at room temperature into 100 parts of water containing 0.5 part of the wetting agent indicated in Example 1. The suspension is treated, while stirring, in the course of 40 minutes with a solution of 3.57 parts of ammonia in 150.3 parts of water and heated to 40°C for 30 minutes. 18.6 parts of the disodium salt of the 4,4' - diaminostilbene - 2,2' - disulfonic acid and a solution of 7.6 parts of sodium bicarbonate in 150 parts of water are subsequently added to the suspension of 2 - amino - 4,6 - dichloro - 1,3,5 - triazine obtained as described above. The mixture is then heated to 75°C for 30 minutes, treated with 13 parts of ethanol-amine and heated to 100°C for a further 45 minutes. The resulting disodium salt of the 4,4' - bis - [2 - amino - 4 - ethanalamino - 1,3,5 - triazinyl - (6) - amino] - stilbene - 2,2' - disulfonic acid is isolated from the

reaction mixture by salting out with sodium chloride.

WHAT WE CLAIM IS:—

1. Process for the production of brightening agents of the bistriazinylaminostilbene series by condensation of 4,4' - diamino - stilbene - 2,2' - disulphonic acid or salts thereof with aminodichlorotriazine compounds of the general formula



wherein R₁ and R₂, independently of each other, stand for a hydrogen atom or for an alkyl or hydroxyalkyl group containing 1 to 5 carbon atoms or for a carboxyalkyl or alkoxy carbonylalkyl group containing 1 to 5 carbon atoms in the alkyl moiety, or jointly with the nitrogen atom, form the morpholine, piperidine or pyrrolidine ring system, in a molecular ratio of 1:2, and optionally subsequently reacting the resulting condensation products with ammonia or amines, characterised by carrying out the condensation of the 4,4' - diamino - stilbene - 2,2' - disulphonic acid or salts thereof with the aminodichlorotriazine compounds in an aqueous medium which is free of organic solvents.

2. Process as claimed in Claim 1, wherein 2 - diethanolamino - 4,6 - dichlorotriazine is used as an aminodichlorotriazine compound.

3. Process as claimed in Claim 1, wherein 2 - N - methyl - ethanalamino - 4,6 - dichlorotriazine is used as an aminodichlorotriazine compound.

4. Process as claimed in Claim 1, wherein 2 - pyrrolidino - 4,6 - dichlorotriazine is used as an aminodichlorotriazine compound.

5. Process as claimed in Claim 1, wherein 2 - amino - 4,6 - dichlorotriazine is used as an aminodichlorotriazine compound.

6. Process as claimed in any of claims 1—5, wherein amino - dichlorotriazine compounds are used in a purified state.

7. Process as claimed in any of claims 1—6, substantially as hereinbefore described in any of the Examples.

8. Brightening agents of the bistriazinyl - aminostilbene series whenever prepared by a process as claimed in any of claims 1—7.

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